

air from the clearances between said individual fibers,

said polymer or oligomer B having a weight average molecular weight of 200 to 50,000,

dispersing said filaments to create clearances between the individual filaments in the matrix, which clearances are substantially filled with said thermoplastic polymer or oligomer B to form a composite A+B with said fibers substantially evenly distributed in said polymer or oligomer B, and

(b) adhering to said composite A+B a thermoplastic polymeric resin C which has a predetermined melt viscosity and a molecular weight of 10,000 or more, and wherein

said thermoplastic polymer or oligomer B has a melt viscosity that is lower than said melt viscosity of said resin C.

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Version with Markings to Show Changes Made to the Specification

Paragraph bridging Pages 3 and 4:

It is also attempted to achieve molding by impregnation of a thermoplastic resin with a reinforcing fiber bundle and dispersion of the fibers simultaneously by molding them into a final product form. This is for increasing the productivity of the thermoplastic composite material in the entire process ranging from the material preparation to molding. When a thermoplastic molding material is molded, usually a relatively high temperature and pressure are applied. For example, in the case of injection molding, the molding material is heated in a cylinder in the plasticization step, and kneaded and pressurized by a screw. Also, in press molding, a high temperature and pressure are also applied. This provides a relatively favorable condition for impregnating a fiber bundle into a thermoplastic resin. The idea of supplying a reinforcing fiber bundle and a high molecular weight thermoplastic resin destined to be a matrix, into a molding machine for achieving impregnation, fiber dispersion and molding simultaneously, has existed for a long time as direct injection molding. According to this method, ~~since~~ it is not necessary to produce a molded material shaped like pellets in which fibers are impregnated with a resin. In such a case it can be considered that the productivity could be greatly improved. However, actually, for example in the case of direct injection molding, impregnation and fiber dispersion are not sufficient. Alternatively, to achieve sufficient impregnation and fiber dispersion, a molding machine having a special screw form to achieve extremely high kneading must be used. So, a general purpose injection molding machine cannot be used, and furthermore, when the material is powerfully or highly kneaded, the desirable long fibers are broken into short fibers by the existing high shearing force, and the molded product cannot manifest the intended high mechanical properties. As described above, there has been no long fiber reinforced thermoplastic

composition material with excellent productivity and excellent molding, and also wherein the product has high mechanical properties.

Page 3, first full paragraph:

The components A and B form a composite. The style of the composite A+B₃ is as shown in Fig. 1, and the clearances between the individual single filaments of its continuous fiber bundle (component A₁) are filled with the component B₁. That is, the component A fibers ₁ are dispersed like “islands in the sea” of the component B₂. Concretely, the component B₂ is thermally molten and impregnated into the component A₁, to form the composite A+B₃.

Page 3, second full paragraph:

Figs. 2 to 7 typically show the forms of sections of the molding materials of the present invention as examples. The form of the section of each molding material is not limited to those illustrated here, so long as the component C₄ is arranged to contact the composite A+B₃. It is preferable that, as shown in Figs. 2 to 5, the component C₄ is arranged to surround the composite A+B₃, or that as shown in Figs. 6 and 7, the composite A+B₃ and the component C₄ are arranged in layers. When a plurality of composite strands ₃ are covered with the component C₄ as shown in Fig. 4, it is desirable that the number of composite strands is 2 to about 6.

Page 3, third full paragraph:

It is desirable that the composite A+B₃ and the component C₄ are bonded at the border. A case where the component C partially penetrates the composite₃ near the border in a compatible condition, or a case where the component C₄ is impregnated into the component A₁ is acceptable.

Page 10, second full paragraph:

For this purpose, it is preferable that, as shown in Figs. 2 to 5, the component C₄ surrounds the composite₃ consisting of the components A₁ and B₂, or that, as shown in Figs. 6 and 7, the composite₃ and the component C₄ are arranged in layers. If the components are arranged as described here, the molding material is able to hold its form since the component C₄ having a high molecular weight surrounds the component B₂ or is arranged on the surface that is likely to be abrasible.

Paragraph bridging Pages 10 and 11:

The component B is a thermoplastic polymer or oligomer having a weight average molecular weight of 200 to 50,000 and a melt viscosity that is lower than that of the component C, and is impregnated into the component A, to form the composite. When the thermoplastic resin having a high viscosity as the matrix is impregnated into the fiber bundle, the component B acts as an impregnation and dispersion aid to help the impregnation and the dispersion of the fibers into the matrix. The reinforcing fiber bundle (component A) is impregnated with the component B that has a low viscosity. So, for example in the step of molding into the final form by injection molding or press molding, etc., when the molding material is heated, pressurized and kneaded, the component B helps the matrix to be impregnated into the fiber bundle (component A) and improves the dispersibility of the reinforcing fibers in the matrix.

Page 13, first full paragraph:

When the molding material in accordance with this invention is produced, the component B is impregnated into the component A beforehand. The component B can be easily impregnated into the continuous fiber bundle (component A), and in the process of continuously impregnating the fiber bundle, the fiber bundle can be run at a high speed of, say, 10 m/min or more, giving excellent productivity. Furthermore, also in the impregnation

process, it is not necessary to use a complicated apparatus for greatly opening the fibers or rubbing the fibers against bars so much as to damage the fibers, or to apply a high pressure to the thermoplastic polymer or oligomer. It is not necessary, either, to adopt a method of low productivity such as diluting the thermoplastic polymer or oligomer for lowering its viscosity for impregnation and then removing the solvent, or producing an emulsion or dispersion for impregnation and then removing the medium. If the impregnation apparatus is optimized, it is achievable that the fiber bundle runs at a speed of tens of meters per minute when the thermoplastic polymer or oligomer (component B) is molten and impregnated, to provide a large advantage that when the molding material is produced, the resin impregnability determines the productivity.

Paragraph bridging Page 16 and 17:

It is desirable that the component A is perfectly impregnated with the component B. Theoretically, if the fibers (component A) are arranged to form a hexagon with the closest packing and the clearances between the fibers are packed with the component B, then the amount of the component B is smallest. If the fibers are assumed to be a complete circle in section and equal in diameter, the volumetric content of the component A is 90.7% ($\pi/(2 \times 3^{1/2})$). It is technically difficult to actually achieve this volumetric content without forming any voids. However, even when a certain quantity of voids exists or when the volumetric content is so high as to form non-impregnated portions in calculation, the present invention has the effect of promoting impregnation and fiber dispersion. Considering that, in order to prevent the mechanical properties of the molded composite material from declining, it is preferable that the volumetric content of the component A in the composite is 40% or more. If the volumetric content exceeds 95%, the clearances between single filaments contain more portions that are not packed with the component B, sharply lowering the impregnation

promoting effect as a result. So, it is preferable that the volumetric content of the component A is 95% or less. A more preferable volumetric content range is 80 to 95%.

Page 17, first full paragraph:

As described before, it is desirable that the component A is perfectly impregnated with the component B, but actually it is difficult. So, the composite consisting of the components A and B ~~contain~~contains some voids. Especially when the component A content is large, more voids exist, and even if some voids exist, the present invention can manifest the effect of promoting the impregnation, and fiber dispersion. However, if the void volume exceeds 40%, the effect of promoting the impregnation and fiber dispersion is remarkably decreased. So, it is preferable that the void volume is 0 to 40%. A more desirable void volume range is 20% or less. The void volume is obtained by measuring the composite portion according to the testing method of ASTM D 2734.

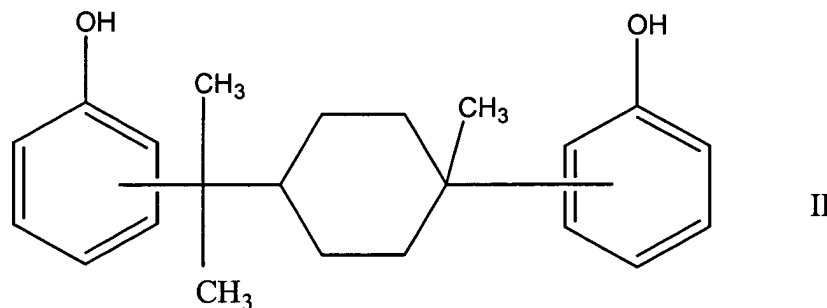
Paragraph bridging Pages 17 and 18:

The surfaces of the reinforcing fibers as the component A are usually treated, considering the adhesiveness to the matrix resin, etc., and furthermore, usually coated with a highly polar coupling agent and sizing agent. For this reason, considering the affinity with the surfaces of the fibers, it is desirable that the thermoplastic polymer or oligomer used as the component B has polar groups. The polar groups include, for example, amino groups, hydroxyl groups, carboxyl groups, etc., and can be selected, considering the affinity with the functional groups, etc. on the fiber surfaces. If the polarity of the matrix resin used as the component C is low, as in the case of a polyolefin, etc., it is desirable that the component B ~~includes~~include portions of an aliphatic hydrocarbon with low polarity, as well as the polar groups. Since the component B is introduced beforehand in the interfaces between the fibers and the matrix, the component B, with both high polar portions and low polar portions, also

functions like a surfactant, and especially contributes to improving fiber dispersibility at the time of molding.

Paragraph bridging Pages 20 and 21:

A composition which is especially excellent as the component B in the molding material of the present invention is such that a product having one molecule of the precursor b added to two molecules of the precursor a (hereinafter called a "2:1 addition product") accounts for 40 wt% or more in the component B. Since one molecule of a low polar aliphatic hydrocarbon is added to two molecules of a high ~~poter~~polar phenol or phenol derivative, the composition as a whole is relatively high in polarity and is excellent in the affinity with a highly polar polyamide with amido groups, etc. It is only required that the 2:1 addition product is contained as a main ingredient in an amount of 40 wt% or more in the component B, and for example, a 1:1 addition product, a 2:2 addition product and other impurities may be additionally present. As an example of the main ingredient of the component B, the molecular structure of the addition product between dipentene as monocyclic monoterpene and phenol is shown in formula II.



Paragraph bridging Pages 21 and 22:

More preferable carbon fibers are 0.05 to 0.4 in the surface chemical function (O/C)

obtained as a ratio of the number of oxygen atoms (O) to the number of carbon atoms on the fiber surfaces measured by the X-ray photoelectron spectroscopy. An O/C ratio of smaller than 0.05 means that the number of functional groups contributing to the adhesion to the matrix resin on the surfaces of the carbon fibers is very small. If the adhesion between the carbon fibers and the matrix resin is poor, the molded product cannot be expected to have high mechanical properties. On the contrary, an O/C ratio of larger than 0.4 means that the surfaces of carbon fibers are oxidized more than required, and that the crystal structure of carbon is destroyed to form a fragile layer on the surface of each fiber. Also in this case, as in the case of too low O/C, destruction is liable to occur near the surface layers of the fibers, and the molded product cannot be expected to have good mechanical properties. If the O/C ratio is kept in the above range, preferable effects can be provided not only for the adhesion at the interfaces between the fibers and the matrix but also for the affinity for impregnation with the component B and the dispersibility of fibers at the time of molding.

Paragraph bridging Pages 23 and 24:

Compounds especially suitable for use as the component C of the molding material of the present invention include polyamides, polyolefins and polycarbonates. Among them, nylon 6, nylon 66 and nylon 6 nylon 66 copolymer have excellent affinity with the oligomer (component B) obtained by condensation of phenol or a phenol derivative and an aliphatic hydrocarbon with two double bonds, and are excellent since the mechanical properties do not decline even after mixing.

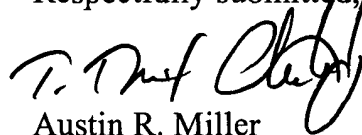
Remarks

We respectfully request that the above-identified amendments be entered into the file of the case. They are made to correct typographical and grammatical errors and no new matter has been added.

New Claim 46 has been added. This claim is identical to Claim 47 which was introduced into parent application Serial No. 09/101,251, restricted by the Examiner and canceled by Examiner's Amendment.

An early and favorable action on the merits of the case is respectfully requested.

Respectfully submitted,



Austin R. Miller
Reg. No. 16,602
T. Daniel Christenbury
Reg. No. 31,750
Attorneys for Applicants

ARM/TDC:dh
(215)563-1810

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In the Claims (clean copy as amended)

Please delete Claims 1-29 and 40-45 without prejudice and without disclaimer of the subject matter contained therein.

Please add the following new claim:

46. (New) A method of making a polymeric composite of a fiber bundle A that has interstices between individual fibers of said bundle A, reinforced by a multiplicity of said fibers in a dispersed condition, and said composite being adapted to be molded into a useful shape,

said method comprising the steps of:

(a) dispersing the fibers of the bundle A by pressing a thermoplastic polymer or oligomer B with a force sufficient to impregnate said fibers with said polymer or oligomer B and substantially fill said interstices with said polymer or oligomer B, while expelling any air from the clearances between said individual fibers,

said polymer or oligomer B having a weight average molecular weight of 200 to 50,000,

dispersing said filaments to create clearances between the individual filaments in the matrix, which clearances are substantially filled with said thermoplastic polymer or oligomer B to form a composite A+B with said fibers substantially evenly distributed in said polymer or oligomer B, and

(b) adhering to said composite A+B a thermoplastic polymeric resin C which has a predetermined melt viscosity and a molecular weight of 10,000 or more, and wherein

said thermoplastic polymer or oligomer B has a melt viscosity that is lower than said melt viscosity of said resin C.

In the Specification (clean copy as amended)

Paragraph bridging Pages 3 and 4:

It is also attempted to achieve molding by impregnation of a thermoplastic resin with a reinforcing fiber bundle and dispersion of the fibers simultaneously by molding them into a final product form. This is for increasing the productivity of the thermoplastic composite material in the entire process ranging from the material preparation to molding. When a thermoplastic molding material is molded, usually a relatively high temperature and pressure are applied. For example, in the case of injection molding, the molding material is heated in a cylinder in the plasticization step, and kneaded and pressurized by a screw. Also, in press molding, a high temperature and pressure are also applied. This provides a relatively favorable condition for impregnating a fiber bundle into a thermoplastic resin. The idea of supplying a reinforcing fiber bundle and a high molecular weight thermoplastic resin destined to be a matrix, into a molding machine for achieving impregnation, fiber dispersion and molding simultaneously, has existed for a long time as direct injection molding. According to this method, it is not necessary to produce a molded material shaped like pellets in which fibers are impregnated with a resin. In such a case it can be considered that the productivity could be greatly improved. However, actually, for example in the case of direct injection molding, impregnation and fiber dispersion are not sufficient. Alternatively, to achieve sufficient impregnation and fiber dispersion, a molding machine having a special screw form to achieve extremely high kneading must be used. So, a general purpose injection molding machine cannot be used, and furthermore, when the material is powerfully or highly kneaded, the desirable long fibers are broken into short fibers by the existing high shearing force, and the molded product cannot manifest the intended high mechanical properties. As described above, there has been no long fiber reinforced thermoplastic

composition material with excellent productivity and excellent molding, and also wherein the product has high mechanical properties.

Page 3, first full paragraph:

The components A and B form a composite. The style of the composite A+B3 is as shown in Fig. 1, and the clearances between the individual single filaments of its continuous fiber bundle (component A1) are filled with the component B1. That is, the component A fibers 1 are dispersed like “islands in the sea” of the component B2. Concretely, the component B2 is thermally molten and impregnated into the component A1, to form the composite A+B3.

Page 3, second full paragraph:

Figs. 2 to 7 typically show the forms of sections of the molding materials of the present invention as examples. The form of the section of each molding material is not limited to those illustrated here, so long as the component C4 is arranged to contact the composite A+B3. It is preferable that, as shown in Figs. 2 to 5, the component C4 is arranged to surround the composite A+B3, or that as shown in Figs. 6 and 7, the composite A+B3 and the component C4 are arranged in layers. When a plurality of composite strands 3 are covered with the component C4 as shown in Fig. 4, it is desirable that the number of composite strands is 2 to about 6.

Page 3, third full paragraph:

It is desirable that the composite A+B3 and the component C4 are bonded at the border. A case where the component C partially penetrates the composite 3 near the border in a compatible condition, or a case where the component C4 is impregnated into the component A1 is acceptable.

Page 10, second full paragraph:

For this purpose, it is preferable that, as shown in Figs. 2 to 5, the component C4 surrounds the composite3 consisting of the components A1 and B2, or that, as shown in Figs. 6 and 7, the composite3 and the component C4 are arranged in layers. If the components are arranged as described here, the molding material is able to hold its form since the component C4 having a high molecular weight surrounds the component B2 or is arranged on the surface that is likely to be abradable.

Paragraph bridging Pages 10 and 11:

The component B is a thermoplastic polymer or oligomer having a weight average molecular weight of 200 to 50,000 and a melt viscosity that is lower than that of the component C, and is impregnated into the component A, to form the composite. When the thermoplastic resin having a high viscosity as the matrix is impregnated in to the fiber bundle, the component B acts as an impregnation and dispersion aid to help the impregnation and the dispersion of the fibers into the matrix. The reinforcing fiber bundle (component A) is impregnated with the component B that has a low viscosity. So, for example in the step of molding into the final form by injection molding or press molding, etc., when the molding material is heated, pressurized and kneaded, the component B helps the matrix to be impregnated into the fiber bundle (component A) and improves the dispersibility of the reinforcing fibers in the matrix.

Page 13, first full paragraph:

When the molding material in accordance with this invention is produced, the component B is impregnated into the component A beforehand. The component B can be easily impregnated into the continuous fiber bundle (component A), and in the process of continuously impregnating the fiber bundle, the fiber bundle can be run at a high speed of,

say, 10 m/min or more, giving excellent productivity. Furthermore, also in the impregnation process, it is not necessary to use a complicated apparatus for greatly opening the fibers or rubbing the fibers against bars so much as to damage the fibers, or to apply a high pressure to the thermoplastic polymer or oligomer. It is not necessary, either, to adopt a method of low productivity such as diluting the thermoplastic polymer or oligomer for lowering its viscosity for impregnation and then removing the solvent, or producing an emulsion or dispersion for impregnation and then removing the medium. If the impregnation apparatus is optimized, it is achievable that the fiber bundle runs at a speed of tens of meters per minute when the thermoplastic polymer or oligomer (component B) is molten and impregnated, to provide a large advantage that when the molding material is produced, the resin impregnability determines the productivity.

Paragraph bridging Page 16 and 17:

It is desirable that the component A is perfectly impregnated with the component B. Theoretically, if the fibers (component A) are arranged to form a hexagon with the closest packing and the clearances between the fibers are packed with the component B, then the amount of the component B is smallest. If the fibers are assumed to be a complete circle in section and equal in diameter, the volumetric content of the component A is 90.7% ($\pi/(2 \times 3^{1/2})$). It is technically difficult to actually achieve this volumetric content without forming any voids. However, even when a certain quantity of voids exists or when the volumetric content is so high as to form non-impregnated portions in calculation, the present invention has the effect of promoting impregnation and fiber dispersion. Considering that, in order to prevent the mechanical properties of the molded composite material from declining, it is preferable that the volumetric content of the component A in the composite is 40% or more. If the volumetric content exceeds 95%, the clearances between single filaments contain more

portions that are not packed with the component B, sharply lowering the impregnation promoting effect as a result. So, it is preferable that the volumetric content of the component A is 95% or less. A more preferable volumetric content range is 80 to 95%.

Page 17, first full paragraph:

As described before, it is desirable that the component A is perfectly impregnated with the component B, but actually it is difficult. So, the composite consisting of the components A and B contains some voids. Especially when the component A content is large, more voids exist, and even if some voids exist, the present invention can manifest the effect of promoting the impregnation, and fiber dispersion. However, if the void volume exceeds 40%, the effect of promoting the impregnation and fiber dispersion is remarkably decreased. So, it is preferable that the void volume is 0 to 40%. A more desirable void volume range is 20% or less. The void volume is obtained by measuring the composite portion according to the testing method of ASTM D 2734.

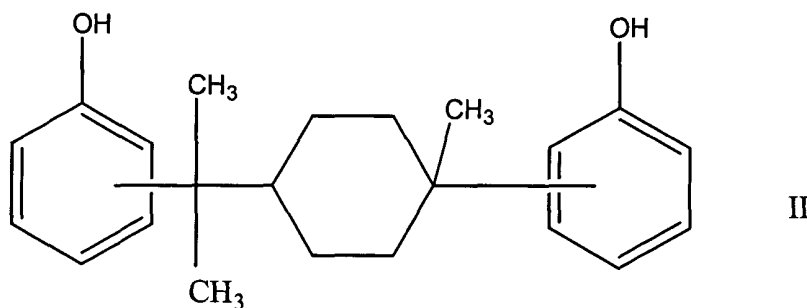
Paragraph bridging Pages 17 and 18:

The surfaces of the reinforcing fibers as the component A are usually treated, considering the adhesiveness to the matrix resin, etc., and furthermore, usually coated with a highly polar coupling agent and sizing agent. For this reason, considering the affinity with the surfaces of the fibers, it is desirable that the thermoplastic polymer or oligomer used as the component B has polar groups. The polar groups include, for example, amino groups, hydroxyl groups, carboxyl groups, etc., and can be selected, considering the affinity with the functional groups, etc. on the fiber surfaces. If the polarity of the matrix resin used as the component C is low, as in the case of a polyolefin, etc., it is desirable that the component B include portions of an aliphatic hydrocarbon with low polarity, as well as the polar groups. Since the component B is introduced beforehand in the interfaces between the fibers and the

matrix, the component B, with both high polar portions and low polar portions, also functions like a surfactant, and especially contributes to improving fiber dispersibility at the time of molding.

Paragraph bridging Pages 20 and 21:

A composition which is especially excellent as the component B in the molding material of the present invention is such that a product having one molecule of the precursor b added to two molecules of the precursor a (hereinafter called a "2:1 addition product") accounts for 40 wt% or more in the component B. Since one molecule of a low polar aliphatic hydrocarbon is added to two molecules of a high polar phenol or phenol derivative, the composition as a whole is relatively high in polarity and is excellent in the affinity with a highly polar polyamide with amido groups, etc. It is only required that the 2:1 addition product is contained as a main ingredient in an amount of 40 wt% or more in the component B, and for example, a 1:1 addition product, a 2:2 addition product and other impurities may be additionally present. As an example of the main ingredient of the component B, the molecular structure of the addition product between dipentene as monocyclic monoterpene and phenol is shown in formula II.



Paragraph bridging Pages 21 and 22:

More preferable carbon fibers are 0.05 to 0.4 in the surface chemical function (O/C) obtained as a ratio of the number of oxygen atoms (O) to the number of carbon atoms on the fiber surfaces measured by the X-ray photoelectron spectroscopy. An O/C ratio of smaller than 0.05 means that the number of functional groups contributing to the adhesion to the matrix resin on the surfaces of the carbon fibers is very small. If the adhesion between the carbon fibers and the matrix resin is poor, the molded product cannot be expected to have high mechanical properties. On the contrary, an O/C ratio of larger than 0.4 means that the surfaces of carbon fibers are oxidized more than required, and that the crystal structure of carbon is destroyed to form a fragile layer on the surface of each fiber. Also in this case, as in the case of too low O/C, destruction is liable to occur near the surface layers of the fibers, and the molded product cannot be expected to have good mechanical properties. If the O/C ratio is kept in the above range, preferable effects can be provided not only for the adhesion at the interfaces between the fibers and the matrix but also for the affinity for impregnation with the component B and the dispersibility of fibers at the time of molding.

Paragraph bridging Pages 23 and 24:

Compounds especially suitable for use as the component C of the molding material of the present invention include polyamides, polyolefins and polycarbonates. Among them, nylon 6, nylon 66 and nylon 6 nylon 66 copolymer have excellent affinity with the oligomer (component B) obtained by condensation of phenol or a phenol derivative and an aliphatic hydrocarbon with two double bonds, and are excellent since the mechanical properties do not decline even after mixing.